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The Choice of the Proper Refractory for the Casting of High Melting Electropositive Metals

Leo Brewer

June 23, 1950

Berkeley, California

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The Choice of the Proper Refractory for the Casting of High Melting Electropositive Metals.

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By

Leo Brewer

As titanium, zirconium, and other of the high melting electropositive metals become more important, the problem of using suitable refractory materials for their casting becomes more important. This paper will discuss the method of choosing and testing possible container materials. To make the discussion more specific, titanium will be used as an example.

As titanium melts at 2000±10°K., it is immediately clear that one is restricted to refractory materials melting considerably above 2000°K. This greatly limits the possible materials that might be considered. The possibility of using any pure high melting element can be quickly eliminated as titanium reacts quite vigorously with non-metals such as carbon and due to its high boiling point and therefore high internal pressure, one can predict that it will dissolve even the most refractory metals. Examination of phase diagrams confirms that even metals such as tantalum, tungsten, and rhenium would not be able to resist attack by titanium.

One is thus limited to high melting compounds such as the oxides, sulfides, nitrides, carbides, silicides, and borides. The first consideration is that, if possible, one would use a compound which is thermodynamically stable in the presence of titanium metal at 2000°K. Titanium should not be able to react with the refractory to form a titanium compound. Thus all compounds less stable than the titanium compound which can exist in equilibrium with titanium metal are excluded.

If one considers possible oxides, first then any oxide used must be more stable than TiO. For TiO, ΔH_{298} = -124 kilocals. Thus any oxide with a heat of formation per gram atom of oxygen not considerably more negative than -124 kilocalories would not be satisfactory. The most stable oxides and their heats of formation at 298°K. are as follows: 1/2 ThO_2, -155 kcals; 1/3 La_2O_3, -152 kcals; CaO, -152 kcals; BeO, -147 kcals; MgO, -144 kcals; Li_2O, -142 kcals. Some of the other third groups oxides are almost as stable as La_2O_3 but will react in a very similar manner. One would not consider an oxide with a heat of formation more positive than -141 kcals. since the reaction Ti(l) + MO(s) = TiO(s) + M(l) would have a ΔH less positive than 17 kilocalories. Since the entropy change for this reaction would be small, the equilibrium constant at 2000°K. would be greater than 10^{-2}. Even if one assumes complete immiscibility of the oxide phases, then one still calculates a mole fraction of M in the titanium melt of over 0.01 taking Raoult's Law for the liquid metals. Due to the high solubility of TiO in titanium metal, the extent of reaction would be even higher. Of the oxides listed above, Li_2O and MgO can be excluded because of the high volatilities of the metals at 2000°K. The reaction of the type Ti(l) + MO(s) = TiO(dissolved in Ti) + M(g) would take place to a large extent and would make these oxides unsuitable. Thus of all the possible oxides, only ThO_2, La_2O_3(or other rare earth oxides), CaO, and BeO would even be seriously considered as a container for molten titanium.

Of these four metals, only Ca boils below 2000°K. Let us consider the magnitude of the reaction Ti(l) + CaO(s) = TiO(dissolved in Ti) + Ca(g). The necessary thermodynamic data for the pure oxides is given by Brewer[1] except for the new heat of formation of TiO obtained by Kelley[2]. Brewer[3] gives

(1) L. Brewer, UCRL-104, July 1948.

(2) K. K. Kelley, U. S. Bureau of Mines, Berkeley, Private Communication, 1950.

(3) L. Brewer, National Nuclear Energy Series, Vol. 19B, Paper 3(1950).

the necessary data for the elements. For the reaction Ti(l) + CaO(s) = TiO(s) + Ca(g), one finds ΔF°_{2000} = 16.5 kcals. Ehrlich[4] reports that samples of Ti and TiO which are equilibrated at high temperature and then cooled to room temperature for x-ray examination show a solid solubility of oxygen in the Ti phase even beyond the composition $TiO_{0.4}$. It is not known at what temperature equilibrium was frozen and the temperature coefficient of solubility is not known, but it will be assumed that the solubility of the TiO phase in Ti metal will be the same at 2000°K. as reported by Ehrlich for his experiments. The phase in equilibrium with Ti metal has the composition $TiO_{0.6}$. The variation of the thermodynamic properties across the TiO homogeneity range are not known. We shall use the data of Darken and Gurry[5] for the FeO homogeneity range as a guide to reasonable estimates for the TiO phase. At 1873°K., the FeO activity changes a factor of almost 6 for a change in the molal ratio of oxygen to iron from 1.012 to 1.37. The type of bonding would be different to some extent in the vicinity of $TiO_{0.6}$ compared to $FeO_{1.012-1.37}$, but we will assume a factor of ten change in the TiO activity upon going from the composition TiO to $TiO_{0.6}$. It is very likely to be smaller than this. Taking this value, we obtain for 1.67 Ti(l) + CaO(s) = 1.67 $TiO_{0.6}$(s) + Ca(g) or 2.5 Ti(l) + CaO(s) = 2.5 $TiO_{0.4}$(l) + Ca(g), ΔF°_{2000} = 7 kcals. This would correspond to 0.24 atm. Ca(g). One would expect very severe attack of CaO by molten titanium under reduced pressures and very extensive attack even under the pressure of inert gas if the rate of approach to equilibrium is rapid which will surely be the case. It is clear that CaO would be expected to be quite unsatisfactory.

Let us now consider the remaining materials, ThO_2, La_2O_3, and BeO. The volatility of the metal should be small for these compounds. There is the

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(4) P. Ehrlich, Z. anorg. Chem., 259, 1 (1949).

(5) L. S. Darken and R. W. Gurry, J. Am. Chem. Soc., 68, 798 (1946).

possibility of lower oxides like ThO and LaO. Reliable data are not available for these compounds in the gaseous state. Gaydon[6] gives ΔH = 161 kcals. for $LaO(g) = La(g) + O(g)$. If this value is correct, reduction of La_2O_3 by Ti to LaO(g) should not be serious. There is no evidence that ThO is very volatile and its evolution as a gas should not cause serious attack. ThO is very difficult to form even when Th metal is used to reduce ThO_2 so it should not be formed when Ti metal is the reducing agent unless it is not necessary to form a pure ThO phase. If ThO can dissolve or react with the TiO phase or the Ti metal, then its formation can be important. The same would apply to the formation of LaO in the condensed phase.

Neglecting this for the moment, let us calculate the extent of attack to be expected if we assume that all products dissolve completely in the titanium metal. $2.5Ti(l) + MO(s) = 2.5TiO_{0.4}(l) + M(l)$ where M is Be, 2/3 La, or 1/2 Th. ΔF°_{2000} = 24 for 1/2 Th, 20 for 2/3 La, and 12 kcals. for Be. If we assume Henry's Law for the solution of oxide in Ti and Raoult's Law for the solution of the metal in Ti, we calculate for thorium a molefraction of 0.005 and for oxygen a molefraction of 0.01. For beryllium, we calculate a molefraction of 0.12 for beryllium and oxygen. Lanthanum falls in between. These calculations tend to indicate more attack than will actually take place if the metal solutions have much of a positive deviation from Raoult's Law. In the cases of La and Th, one might well expect a positive deviation. It is difficult to predict the behavior of Be in Ti.

These calculations are very rough, but in any case it is clear that even with the most stable oxide refractories available, we can expect contamination at least of the order of one mole percent. If the casting is done quickly so that equilibrium is not attained, it might be possible to lower these values.

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(6) A. G. Gaydon, Dissociation Energies, Chapman and Hall, London (1947).

In the calculations, it was assumed that La_2O_3, ThO_2, and BeO were the phases of narrow homogeneity range. Actually they must have appreciable ranges. The above calculations apply to the oxide phases which have been reduced to the metal high end of their homogeneity range. The calculations would not apply to oxide refractory containers prepared by firing in air. Such containers would give up oxygen quite readily to the titanium metal until they were reduced to the lower end of their homogeneity range.

Since oxide containers do not appear highly promising, we might consider whether other compounds might possibly be more satisfactory. If all elements fell in the same order in regard to their electropositive character, regardless of the type of solution or compound considered, then it is clear that the most electropositive element would reduce compounds of all other elements and could not be contained under conditions where approach to equilibrium is rapid. Fortunately, the order of stability of compounds of the various elements vary greatly with the type of compound. Tables I, II, III, and IV show how the heats of formation per equivalent of iodides, fluorides, oxides, and sulfides vary with position in the periodic table. Only elements of the left hand side of the extended periodic system are considered because all compounds further to the right are much less stable. The data in the tables were obtained from Brewer, Bromley, Gilles, and Lofgren[7], Brewer[1], and Brewer, Bromley, Gilles, and Lofgren[8].

Examination of Table I shows that the region of greatest stability for the iodides is the lower left hand corner of the periodic table at Cs and Ti is

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(7) L. Brewer, L. A. Bromley, P. Gilles, and N. L. Lofgren, Nat. Nuclear Energy Series, Vol. 19B, Paper 6 (1950).

(8) L. Brewer, L. A. Bromley, P. Gilles, and N. L. Lofgren, Nat. Nuclear Energy Series, Vol. 19B, Paper 4 (1950).

Table I

ΔH_{298} of formation from $I_2(g)$ in kcals/gram atom iodine.

LiI -72.5	1/2 BeI_2 -27.2	1/3 BI_3 -17.
NaI -76.7	1/2 MgI_2 -50.9	1/3 AlI_3 -33.
KI -86.3	1/2 CaI_2 -71.7	1/3 ScI_3 -50.
RbI -88.4	1/2 SrI_2 -75.5	1/3 YI_3 -55.
CsI -91.3	1/2 BaI_2 -79.8	1/3 LaI_3 -63.

Table II

ΔH_{298} of formation in kcals/gram atom fluorine.

LiF -145.6	1/2 BeF_2 -113.5	1/3 $BF_3(g)$ -91.
NaF -136.0	1/2 MgF_2 -131.5	1/3 AlF_3 -108.
KF -134.5	1/2 CaF_2 -145.1	1/3 ScF_3 -122.
RbF -133.2	1/2 SrF_2 -144.5	1/3 YF_3 -132.
CsF -131.7	1/2 BaF_2 -143.	1/3 LaF_3 -140.

Table III

ΔH_{298} of formation in kcals/gram atom oxygen.

Li_2O	BeO	$1/3 B_2O_3$		
-142.3	-147.	-101.2		
Na_2O	MgO	$1/3 Al_2O_3$	$1/2 SiO_2$	
-102.9	-143.8	-133.0	-104.	
K_2O	CaO	$1/3 Sc_2O_3$	$1/2 TiO_2$	TiO
-86.2	-151.7	-147.	-112.8	-124.2
Rb_2O	SrO	$1/3 Y_2O_3$	$1/2 ZrO_2$	
-82.9	-140.8	-150.	-129.5	
Cs_2O	BaO	$1/3 La_2O_3$	$1/2 HfO_2$	
-82.1	-133.	-152.	-135.8	
			$1/2 ThO_2$	
			-155.	

Table IV

ΔH_{298} of formation from $S_2(g)$ in kcals/gram atom sulfur.

	BeS	$1/3 B_2S_3$		
	-71.	-37.		
Na_2S	MgS	$1/3 Al_2S_3$	$1/2 SiS_2$	
-105.3	-99.9	-114.	-32.5	
K_2S	CaS			
-103.4	-128.9			
Rb_2S	SrS			
-103.	-128.6			
Cs_2S	BaS	$1/3 Ce_2S_3$		
-102.	-126.7	-115.7		
		CeS	$1/2 ThS_2$	ThS
		-133.4	-85.	-120.

very far from the region of maximum stability. Thus Ti does not easily reduce the most stable iodides. It will be noted that stability decreases as one moves upward or to the right in the periodic table.

Table II shows a much different behavior. The region of maximum stability is a ridge extending from Li to Ca to La and stability falls off on either side of this line. The behavior of the alkali compounds is especially striking. While the stability of the iodides increases from LiI to CsI, the reverse is true for the fluorides.

Table III for the oxides shows a behavior very similar to that of Table II. One has a ridge of maximum stability stretching from Li to Th. Table IV also shows such a ridge for the sulfides, but it has been lowered somewhat. Also the third group elements form stable dipositive sulfides whereas no such phases are stable in the oxide systems.

Thus in fluoride and oxide systems, Ti is relatively a more powerful reducing agent than it is in iodide or sulfide systems. Our object then is to find a series of refractory compounds which has the region of maximum stability as far away as possible from titanium.

Let us examine the factors which determine the region of maximum stability and attempt to predict the region of maximum stability for carbides, silicides, nitrides, and borides. To properly understand the variation of a function as complicated as a heat of formation, it is usually most convenient to divide it up into the various terms of the Born-Haber cycle as Brewer, Bromley, Gilles, and Lofgren[7] have done in Appendix 1 of their paper. Their paper and the accompanying papers give all the necessary data required for the Born-Haber cycle. Let us now consider the various terms which affect the stability of alkali metal compounds. First there is the heat of sublimation of the metal which decreases from lithium to cesium and therefore tends to make

the stability of the compounds increase in the same order. Also the ionization potentials of the gaseous atoms decrease from lithium to cesium and therefore tend to make cesium compounds more stable than lithium compounds. The only other term which varies when the alkali metal is varied is the lattice energy of the compound. The lattice energy will vary roughly inversely with the interionic distance or the distance from center to center of the ions. Thus the increase in size from lithium to cesium decreases the lattice energy and tends to make cesium compounds less stable than lithium compounds. Thus the trend to be expected depends upon which shows the greatest variation from lithium to cesium - the lattice energy or the sum of the heats of sublimation and ionization. This depends upon the size of the anion. When the anion is large like iodide ion, then the fractional change in the interionic distance in going from LiI to CsI is rather small compared to the fraction change in the interionic distance in going from LiF to CsF. Thus the variation of heats of sublimation and ionization outweighs the lattice energy variation for the iodides and the stability increases as one goes from lithium to cesium. In the case of the fluorides, the lattice energy variation is largest and the stability of the compounds decreases as one goes from lithium to cesium. In addition to the fractional change in the interionic distance affecting the percent change in the lattice energy, another important factor affecting the lattice energy is the cation-anion radius ratio. When the cation-anion ratio is quite small as in lithium iodide for example the lattice energy is reduced due to the crowding of the large anions. The anion-anion repulsion prevents the anions from approaching the cation as closely as they might like and the effective interionic distance is greater than the sum of the ionic radii. Thus the lattice energy does not increase as rapidly as one might expect as one reduces the cation size. A large reduction in the cation-anion ratio will ultimately lead to a reduction in coordination number which will also result in a lower lattice energy. The radius ratio effect supports the normal

trend in the case of the iodides which results in a higher stability for CsI relative to the elements than for LiI. In the case of the fluorides, the anion repulsion effect is not important due to the small size of fluoride ion.

Thus whenever the anion is large compared to the cation, we will expect the heats of sublimation and ionization to fix the trend in stability of the compounds which will normally result in an increase in stability as one descends in the periodic table or as one moves to the left. When the anion is not much larger than the cation, then one would expect a reversal. One can expect to find a critical ratio for which small cations would show the normal trend in stability while larger cations would show the so-called abnormal decrease in stability as one descends in the periodic table.

If one carries the above reasoning over to analysis of the data for the halides, oxides, and sulfides of the alkali metals, alkaline earth metals, etc., one can find a ready explanation for the trends in the heats of formation which are noted in Tables I, II, III, and IV. Thus if we examine column two of Table II, we find the normal increase in stability as one descends in the periodic table from Be to Ca where one reaches a maximum and then the stability decreases from Ca to Be. There is enough anion repulsion for cations smaller than Ca to produce the normal trend. For larger cations, the decrease in lattice energy outweighs the change in ionization potential.

As the size of the cation decreases with increase in charge, one would expect the change from normal trend to abnormal trend to occur lower and lower in the table as one increases the charge of the cation. Thus in Table II, we see that even at Li, the cation is not small enough to have given us a reversal in the trend. With the dipositive ions, the maximum is reached at Ca and with the tripositive ions, the maximun is reached at lanthanum or lower. The tetrapositive compounds show the normal continuous increase in stability

as the size of the cation is increased. The same is observed for the oxides where the anion is also small. Thus we see the explanation for the ridge of maximum stability extending from Li to Ca to La to Th for the fluorides and oxides, whereas the large halides have their region of maximum stability in the lower left hand corner of the periodic table.

It is of interest to note the effect of replacing oxide ion by the larger sulfide ion. In going from sodium to cesium, the oxide stability decreased by 21 kilocals. The sulfide stability decreased only by 3 kilocals. The larger sulfide ion has almost wiped out the abnormal decrease in stability as one descends in the periodic table. One would predict that the selenides will show an increase in stability from lithium to cesium. In the alkaline earth column, the effect of anion repulsion is seen clearly in comparing the trend from beryllium to calcium for both the oxides and sulfides. The maximum for the sulfides is between calcium and strontium.

If we now consider the series F, O, N, C, and B, we would expect if the bonding remained largely ionic that the ridge observed for the fluorides and oxides would remain in roughly the same position. If general arrangement and sizes remained the same, there would be no change in the lattice energy upon replacing the singly charge F^- ions by half as many doubly charged $O^=$ ions. The sizes should not vary greatly as long as one remains in the same horizontal row of the periodic table. However, it is clear from many indications that the bonding does not remain so largely ionic when one has reached the carbides and borides as one moves to the left in the table from fluorine and oxygen. It is clear that the extra "d" electrons are participating in bonding of the carbides and thus there tends to be an increasing stability of the lattice due to increasing contribution of metallic bonding as one moves from the extreme left of the table toward the platinum metals.

This tends to move the ridge of maximum stability to the right. The theory of the bonding in carbides is not well enough advanced to predict the exact location of the region of maximum stability. However, we may examine the available data on the heats of formation of nitrides and carbides as given by Brewer, Bromley, Gilles, and Lofgren[8]. The data are rather incomplete and not too reliable. The nitrides show a ridge of maximum stability somewhat similar to the oxides but moved upward and to the right. It extends from Be to La to Zr to U. It is at least clear from the rapidity with which the heats of formation are falling off as one moves away from the ridge of maximum stability that one is not likely to find any useful refractories outside of this narrow region of maximum stability. A detailed analysis of the lattice energies of the nitrides indicates that the bonding is largely ionic for the first three groups; so one might venture to predict that the phosphide will have their region of maximum stability lower in the table. It is clear that the nitrides would not be suitable as containers for titanium since titanium falls so close to the region of maximum stability. The phosphides would be more practical than the nitrides just as the sulfides would be more practical than the oxides since the region of maximum stability is farther removed from titanium.

The data for the carbides are even more incomplete, but the region of maximum stability appears to be in the neighborhood of Ta. The value given for TiC appears out of line and it is likely that the values for Zr and Th should indicate much greater stability.

No quantitative data for the borides or silicides exist, but the qualitative data available give every indication that a similar region of maximum stability exists and only the compounds from a very limited area of the periodic table would fall within this region. It is not possible to predict

whether titanium would be further away from the region of maximum stability of the borides and silicides than it is from the regions of maximum stability of the sulfides and carbides. However, it is clear that the oxides and nitrides would not be expected to provide satisfactory materials. One would hope to find the most satisfactory container materials from the regions of maximum stability of the borides, silicides, carbides, and sulfides. From the work of Brewer, Searcy, Templeton, and Dauben[9] on the silicides, the work of Brewer, Sawyer, Templeton, and Dauben[10] on the borides, and the work of Eastman, Brewer, Bromley, Gilles, and Lofgren[11] on the sulfides, this would limit one to the following compounds: $Ta_5Si_{1\pm0.2}$, Mo_3Si, TaB, ZrB_4, UB_2, CeB_4, CeS, ThS, $TaC_{0.8-1.0}$ or compounds of elements very close by in the periodic table, although further considerations are necessary before they can be recommended.

Let us consider possible reactions of titanium metal with the above compounds. The above discussion about relative stabilities of compounds was based on heats of formation from the solid metals. The order of stability would be greatly changed if the stabilities were considered from the gaseous metals. However, all of the above refractories are compounds of relatively non-volatile metals; so we do not have to consider the possibility of reduction by titanium to form the volatile metallic element as we had to in

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(9) L. Brewer, A. Searcy, D. H. Templeton, and C. H. Dauben, paper accepted by J. Amer. Ceramic Soc., 1950.

(10) L. Brewer, D. L. Sawyer, D. H. Templeton, and C. H. Dauben, paper submitted to J. Amer. Ceramic Soc., 1950.

(11) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, J. Am. Chem. Soc., 72, 2248 (1950); additional paper on thorium sulfides accepted by J. Am. Chem. Soc. (1950); and paper on sulfide crucibles submitted to J. Amer. Ceramic Soc. (1950).

the cases of alkali and alkaline earth oxides. Also for all of these compounds, it is believed that stable gaseous molecules are of no importance; so there can be no reduction to volatile compounds of lower oxidation state as was possible with some of the oxides. Therefore there are two main reactions we will want to consider. Titanium might reduce these compounds to solid phases of lower oxidation number or it might disproportionate these compounds to remove some of the metal and form a compound of higher oxidation number. These two reactions are illustrated by known reactions in other systems. Thus $2Pt + 4CeS = CePt_2 + Ce_3S_4$ and $Ce_3S_4 + Ba = BaS + 3CeS$.

Starting with the sulfides, we might consider the possibility of this type of reaction with titanium. There is no indication in the literature of any very stable intermetallic compound formed between Ti and Ce or Th. Therefore, it is not likely that Ti will cause any appreciable disproportionation. No phases of lower oxidation number are known in the sulfide systems; so no reduction would be expected.

In the Ta-C system, there is a lower phase, Ta_2C, and one might expect reduction of TaC to Ta_2C by Ti. However, the TaC forms a solid solution with TiC which would stabilize TaC with respect to Ta_2C. Ta_2C is just barely stable with respect to TaC and it does decompose at high temperatures peritectically. Therefore, in the presence of Ti, one would expect Ta_2C to be unstable by disproportionation, but TaC should be stable and is therefore the phase to use. This could be easily checked by heating Ta_2C with Ti and TaC with Ti.

Since $Ta_5Si_{1\pm0.2}$ is the silicide of lowest oxidation number in the Ta-Si system, it should not be reduced by Ti to a lower phase. There is no indication that it disproportionates easily, but there is the possibility that Ti could cause its disproportionation. This could be easily determined

by mixing Ti powder with the powdered silicide. If it does disproportionate, then $Ta_5Si_{2\pm0.5}$ would be the phase to use as a container. Mo_3Si appears to be in the same position as $Ta_5Si_{1\pm0.2}$.

Among the borides suggested above, CeB_4, ZrB_2, and UB_2 are the phases of lowest oxidation state known for the system. There is no indication of ready disproportionation; so they should not undergo either of the reactions being considered. TaB is not the lowest boride of the tantalum system, but the lower borides all disproportionate readily and should be unstable in the presence of titanium metal.

After having tested the stability of the phase to be used as a container, one must be sure that there is not partial reduction with no phase change. Thus if TaC were used as a container, one could be sure that titanium would react with it to reduce the carbon to metal ratio since there is a homogeneity range from $TaC_{0.8}$ to $TaC_{1.0}$. Therefore, each of the phases suggested above should be at the lower end of its homogeneity range in order to minimize reduction. Also there may be some solubility of titanium carbide, sulfide, etc. in the corresponding container material. This would produce a tendency of the titanium to react to overcome the unsaturation. This would have to be prevented by including enough titanium in the container material to saturate it. The simplest way to insure that the container material is at the lower end of its homogeneity range and is saturated with titanium is to heat the finely divided refractory material intimately mixed with titanium powder and to determine by x-ray examination the composition of the phase in equilibrium with titanium liquid. This would be done comparison of the observed lattice constant after treatment with the lattice constant of phases of known composition.

If the following procedures were followed, then one would have boride,

silicide, carbide, and sulfide container materials which would be in equilibrium with titanium liquid and which would not take up any titanium. Under those conditions the only limitation to their success would be the solubility of the refractory in the titanium metal. Some tantalum and silicon, for example, would have to dissolve in the titanium for the titanium to be in equilibrium with the container. If the container material is stable enough and high-melting enough, there is a good chance that this solubility will be low. Also the rate of solution may be quite small if the container material has been stabilized by preparation of the proper composition as discussed above.

Summary

It is very unlikely that Ti can react with any of the phases suggested above as container materials to form either a new titanium phase or a new ternary phase. If the container material has been stabilized by prior treatment with titanium before fabrication so as to be saturated with respect to titanium, the container material should not react with the titanium in any way except for some solubility of the constituents directly in the titanium metal. If one constituent is dissolving to a greater extent than the other, for example more Ta than Si from a tantalum silicide, it is possible to decrease the solubility by taking a different concentration in the ternary Ta-Si-Ti homogeneity range with a lower Ta content. This would increase the solubility of the Si in the titanium metal, but the total contamination could be reduced. As thermodynamic data are not available for the borides, silicides, or sulfides of titanium, it is not possible to make thermodynamic calculations to predict the equilibrium solubility of the

stabilized container material in titanium metal. Ehrlich[4] reports the solubility limits of the lowest phases of the hydrogen, oxygen, nitrogen, carbon, and boron systems of titanium in titanium metal. The solubilities of the phases suggested as container materials should be considerably less than the solubilities of the pure titanium compounds. If the non-metal is particularly undesirable in the titanium metal, it can be decreased by going to the edge of the homogeneity range where it is lowest. Its reduction would be at the expense of increase in the metallic impurity.

The above phases offer the best chance of finding a container material which will be thermodynamically stable against attack by titanium metal. However titanium is rather close to the region of maximum stability of the compounds in every case, and it is possible that the equilibrium solubility of the container material in molten titanium will be excessive.

It is recommended that these materials be tried first under conditions which make the reaction with titanium go as completely as possible. That is, the powdered container material should be intimately mixed with Ti powder and taken to 2000°K. The results of experiments of that type will greatly expedite the choice of a proper container material.

Experiments in which Ti metal is heated in a fabricated crucible are not very satisfactory for preliminary studies. Impurities in the crucible may often lead one to wrong conclusions about the crucible material. ThS normally contains a considerable amount of ThO_2 impurity. Thus Ti heated in a ThS crucible will dissolve oxygen and a test of the crucible which merely relies upon measurement of the hardness or some general property of the metal which can be affected by any impurity does not indicate the behavior of ThS. Experiments with intimately mixed materials will give one a much better idea whether the crucible material has been affected. Also

it is easier to obtain the material purer in powdered form than in the form of a fabricated crucible. Another objection to the use of fabricated crucibles in preliminary work is that any material will contaminate an electropositive metal if it is not at the reduced end of its homogeneity range. One must make preliminary studies with powders to determine what compositions in the homogeneity range should be used for fabrication of the crucible.

Such preliminary studies with powders require some container for the powdered mixtures. If available, the refractory material can be used as a container. Thus if one is studying the reaction between finely divided Ti and BeO powders, one would use a BeO crucible. If the same refractory material is not available, one can use some other refractory material since the reaction between the powders will be much more rapid than the reaction with the crucible. The interior of the powder can be examined to minimize effect of the container.

In studies of the extent of attack of various materials, one should know the effect of various materials upon the properties of titanium. Some of the suggested refractory materials may dissolve to some extent in molten titanium metal but will precipitate so completely upon cooling that the titanium phase will be quite pure and the titanium might not be hardened for example. If the refractory material present as intergranular material does not harm the properties of titanium metal, then of course the refractory material would make a better container than some other material which dissolves to a smaller extent but remains dissolved in the titanium and causes a greater change in the properties of the titanium metal.